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# Nuclear Quantum Vibrational Effects in Shock Hugoniot Temperatures

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## Abstract.

We present a straightforward method for the inclusion of quantum nuclear vibrational effects in molecular dynamics calculations of shock Hugoniot temperatures. Using a Grüneisen equation of state and a quasi-harmonic approximation to the vibrational energies, we derive a simple, post-processing method for calculation of the quantum corrected Hugoniot temperatures. We have used our novel technique on *ab initio* simulations of shock compressed water. Our results indicate significantly closer agreement with all available experimental temperature data. Our formalism and technique can be easily applied to a number of different shock compressed molecular liquids or solids.

**Keywords:** Hugoniot temperature, molecular dynamics, quantum effects

## INTRODUCTION

Measurement of shock Hugoniot temperatures of many systems remains an unresolved issue[1]. Accurate temperatures remain difficult to determine due to large uncertainties in the calibration of pyrometric measurements[1, 2]. As a result, experiments tend to rely on equation of state models for temperature data, which have been shown to be inaccurate for some systems[2]. Molecular Dynamics (MD) simulations provide an independent route to temperature determination, where material properties such as the shock Hugoniot states are readily computed[3, 4].

Accurate modeling of the breaking and forming of chemical bonds in MD simulations usually requires the use of quantum theories such as Density Functional Theory (DFT)[5, 4]. However, DFT-MD simulations have been shown to under-predict experimental Hugoniot temperatures for covalently bonded materials by up to 20 – 30%[6, 4]. Molecular Dynamics simulations in general propagate classical nuclear equations of motion, neglecting quantum zero-point and vibrational energy effects. As a result, the erroneous classical heat capacities inherent in MD simulations of these materials could produce Hugoniot temperatures that are too low. Determination of

material equations of state could be greatly facilitated by a more accurate MD temperature calculation methodology that includes these quantum effects. In this work, we report a novel theoretical post-processing methodology for the inclusion of quantum nuclear vibrational effects in the equation of state from MD simulations of shock compression.

## METHODS

We first approximate the equation of state of the true (quantum) system by using a Grüneisen equation of state[7]:

$$E(V, T) = E_c(V) + E_T(V, T) \quad (1)$$

$$P(V, T) = P_c(V) + P_T(V, T) \quad (2)$$

Here, the quantities  $E_c$  and  $P_c$  correspond to the cold components of the internal energy and pressure, respectively, which are independent of temperature.  $E_T(V, T)$  corresponds to the thermal component of the internal energy. The thermal component of the pressure is defined as  $P_T \equiv \Gamma(V)E_T(V, T)/V$ , where  $\Gamma(V)$  is the dimensionless Grüneisen coefficient. The

Grüneisen parameter  $\Gamma(V)$  is assumed to be independent of temperature in the equation of state. The cold and thermal portions of the internal energy can be written in terms of their electronic ( $el$ ) and ionic ( $i$ ) components:

$$E_c(V) = E_c^{el}(V) + E_c^i(V) \quad (3)$$

$$E_T(V, T) = E_T^{el}(V, T) + E_T^i(V, T). \quad (4)$$

For this work, our MD simulations are all in the electronic ground-state, i. e.,  $E_c^{el}(V)$ , which allows us to neglect electronic contributions to the thermal energy ( $E_T^{el}(V, T) = 0$ ). Regardless, we include  $E_T^{el}(V, T)$  in our formalism, although our final expression for the difference between the quantum and classical thermal energy will depend exclusively on the ionic components to  $E_T$  and  $E_c$ .

In first principles Molecular Dynamics, the ions are treated classically, and we denote the equation of state for the classical system with lower case letters:

$$e(V, t) = e_c(V) + e_T(V, t) \quad (5)$$

$$p(V, t) = p_c(V) + \Gamma(V)e_T(V, t)/V, \quad (6)$$

where  $e$ ,  $p$ , and  $t$  represent the classical internal energy, pressure and temperature, respectively, we have substituted in the definition of the thermal component of the pressure in Eqn. 6, and  $\Gamma(V)$  is the same Grüneisen coefficient, mentioned above. Here, the volumes of the quantum and classical systems are constrained to be the same. For the classical system the cold energy is entirely electronic, viz.,

$$e_c(V) = E_c^{el}(V). \quad (7)$$

Inclusion of electronic thermal effects yields the following for the classical thermal energy:

$$e_T(V, t) = E_T^{el}(V, T) + e_T^i(V, t). \quad (8)$$

We now assume that the vibrational density of states and electronic energies ( $E_c^{el}$  and  $E_T^{el}$ ) are the same in both systems. Consequently, the Grüneisen coefficients are also the same for both classical and quantum systems. We constrain both systems to have the same initial pressure  $P_0$  and temperature  $T_0$ . We ignore the contribution of zero-point vibrations to the cold component of the pressure  $P_c^i(V)$ , which we estimate to be smaller than the error bars in our computed stress. As a result, we have  $p_c(V) = P_c(V)$ .

For a shock compressed process, both quantum and classical systems will satisfy the Hugoniot relation:

$$E(V, T) - E(V_0, T_0) = \frac{1}{2}(V_0 - V)(P + P_0) \quad (9)$$

$$e(V, t) - e(V_0, T_0) = \frac{1}{2}(V_0 - V)(p + P_0). \quad (10)$$

Using equations 1 and 2, we can then expand equation 9 as the following:

$$E_c(V) - E_c(V_0) + E_T(V, T) - E_T(V_0, T_0) = \frac{1}{2}(V_0 - V) \left[ P_c(V) + \frac{\Gamma(V)E_T(V, T)}{V} + P_0 \right]. \quad (11)$$

Expanding the cold energy  $E_c(V)$  and the thermal energy  $E_T(V, T)$  into their electronic and ionic parts, and solving for  $E_T^i(V, T)$ , we obtain:

$$E_T^i(V, T) = \frac{E_T(V_0, T_0) - \Delta E_c^{el} - \Delta E_c^i + \frac{1}{2}(P_c(V) + P_0)(V_0 - V)}{\left[ 1 - \frac{\Gamma(V)(V_0 - V)}{2V} \right]} - E_T^{el}(V, T), \quad (12)$$

where  $\Delta E_c^{el} = E_c^{el}(V) - E_c^{el}(V_0)$  and  $\Delta E_c^i = E_c^i(V) - E_c^i(V_0)$ .

Similarly, for the classical system, we obtain:

$$e_T^i(V, t) = \frac{e_T(V_0, T_0) - \Delta E_c^{el} + \frac{1}{2}(P_c(V) + P_0)(V_0 - V)}{\left[ 1 - \frac{\Gamma(V)(V_0 - V)}{2V} \right]} - E_T^{el}(V, T). \quad (13)$$

We then subtract Eqns. 12 and 13 to obtain the following relation for  $E_T^i(V, T)$ :

$$E_T^i(V, T) = e_T^i(V, t) + \frac{[E_T^i(V_0, T_0) - e_T^i(V_0, T_0)] - \Delta E_c^i}{\left( 1 - \frac{\Gamma(V)(V_0 - V)}{2V} \right)} \quad (14)$$

which we simplify to

$$E_T^i(V, T) = e_T^i(V, t) + \Delta E_{T-c}(T_0, V_0; V), \quad (15)$$

where  $\Delta E_{T-c}(T_0, V_0; V)$  equals the second term on the right hand side of Eqn. 14.

In order to compute the values of the cold and thermal quantum ionic energies,  $E_c^i(V)$  and  $E_T^i(V, T)$ , we apply the quasi-harmonic approximation to the

vibrational states of the system. As a result, we write the cold ionic energies as:

$$E_c^i(V) = \frac{1}{2} \int_0^\infty \rho(\omega, V) \hbar \omega d\omega, \quad (16)$$

where  $\rho(\omega, V)$  is the vibrational density of states of the system, which we take to be the power spectrum of the time dependent velocity autocorrelation function, viz.,  $\rho(\omega, V) \propto \int_0^\infty d\tau \cos(\omega, \tau) \langle \mathbf{v}(\tau) \mathbf{v}(0) \rangle / \langle \mathbf{v}(0)^2 \rangle$ . We normalize  $\rho(\omega, V)$  to  $\int_0^\infty d\omega \rho(\omega, V) = 3N_A$ , where  $N_A$  equals Avogadro's Number. With this definition  $E_T$  below has units of energy/mol, and  $V$  is a molar volume.

Similarly, we write for  $E_T^i(V, T)$ :

$$E_T^i(V, T) = \int_0^\infty d\omega E_{QHO}^T(\omega, T) \rho(\omega, V) \quad (17)$$

where  $E_{QHO}^T(\omega, T)$  is the average thermal energy of the quantum harmonic oscillator:

$$E_{QHO}^T(\omega, T) = \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}. \quad (18)$$

We now relate  $E_T^i(V, T)$  and  $e_T^i(V, t)$  by taking Eqns. 17 and 15 to form:

$$\begin{aligned} E_T^i(V, T) &= \int_0^\infty d\omega E_{QHO}(\omega, T) \rho(\omega, V) \\ &= 3Nk_B t + \Delta E_{T-c}(T_0, V_0; V). \end{aligned} \quad (19)$$

Thus, determination of the Hugoniot quantum temperature proceeded as follows. After calculation of the power spectrum, we use Eqns. 16 and 17 to determine the value of  $\Delta E_{T-c}(T_0, V_0; V)$ . Values of  $\Gamma(V)$  were computed by first performing two constant volume-temperature (NVT) simulations at the Hugoniot temperature and at 200 K above for both the lowest and highest simulation densities for each system.  $\Gamma(V)$  was then determined by using the relation  $\Gamma(V) = V(\frac{\partial P}{\partial E})_V \approx V(P_2 - P_1)/(E_2 - E_1)$ . Values of  $\Gamma(V)$  at densities between the two extrema were computed via linear regression. We then use Eqn. 19 to solve iteratively for the quantum Hugoniot temperature  $T$ , which we label  $T_{QM}$ . Since the power spectrum can be calculated for any saved simulation trajectory, our technique can easily be applied to any previously computed shock compression MD simulation.

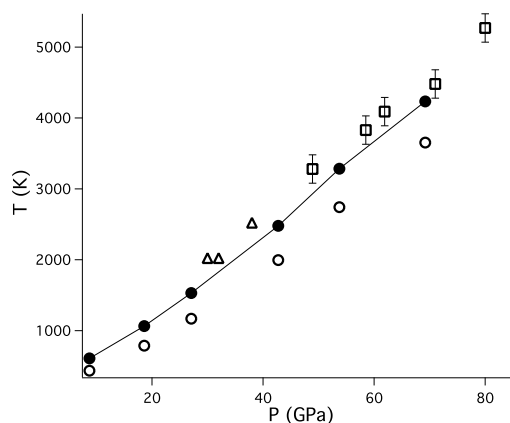
## COMPUTATIONAL DETAILS

All shock compression simulations were conducted with the Multi-Scale Shock Technique (MSST)[8]. MSST can dramatically reduce the number of particles relative to non-equilibrium molecular dynamics (NEMD) methods, while guaranteeing that the simulation converges to the correct thermodynamic end state. The MSST [8] maintains the system on *both* the Rayleigh line  $p - p_0 = U^2(v_0 - v)/v_0$ , (where  $U$  is the shock velocity) and the shock Hugoniot under condition of uniaxial strain of the computational cell. By regulating the strain rate of the computational cell, we guarantee that the  $(P, T)$  thermodynamic states accessed during the shock simulation correspond to a steady macroscopic shock wave. This allows for much smaller system sizes to be used to achieve the same results as standard Non-Equilibrium Molecular Dynamics simulations[9]. MSST has been used in conjunction with DFT-MD to accurately reproduce the shock Hugoniot of a number of systems[4].

Our simulations of shock compressed water have been discussed in a previous publication[4]. We used the CPMD simulation software package[10] with Born-Oppenheimer Molecular Dynamics. Stronger shock velocities resulted in electronic excitation beyond the Born-Oppenheimer state, which requires the inclusion of electron thermal excitations[11]. We performed six simulations with shock velocities from 5 to 11 km/s, each with a time step of 0.1935 fs and for up to 11 ps. All simulations were started from the same configuration taken from an equilibrated CPMD simulation of 64 H<sub>2</sub>O at ambient conditions.

## RESULTS AND DISCUSSION

Our results for the Hugoniot temperature values for water are shown in in Fig. 1. Using the method for approximation for  $\Gamma(V)$  mentioned above, we computed values of  $\Gamma = 0.681$  at 8.3 GPa (5 km/s) and  $\Gamma = 0.355$  at 67.8 GPa (11kms). These results are similar to experimental values for  $\Gamma$  for water at lower pressures and temperatures[12]. We have shown excellent agreement of our simulations with experimental results for the pressure vs. density equation of state of water[4]. We find that our quantum mechanical corrections bring our calcu-



**FIGURE 1.** Plot of classical and quantum Hugoniot temperatures for water. Open circles correspond to classical ionic temperatures, and solid circles to quantum corrected temperatures. Experimental results are labeled with open triangles [13] and open squares[2].

lated temperatures in excellent agreement with experiment. Our results show that quantum nuclear vibrational effects play a significant role in water even at elevated temperatures ( $> 4000$  K).

## CONCLUSIONS

Our quantum Hugoniot temperature calculation method yields an improved agreement between DFT-MD simulations and pyrometry experiments. We predict significant quantum corrections to the Hugoniot temperatures of our simulations, due to quantization of the high frequency vibron of covalently bonded systems such as water. Our technique is independent of the model used for MD simulation, and can easily be applied to any number of systems including complicated mixtures. Our quantum Hugoniot temperature method can also be used to compute Hugoniot temperatures where equation of state modeling is known to be inaccurate.

Prior to our submission, we were made aware of recent results from a somewhat similar technique used to calculate the influence of quantum nuclear vibrational effects on the equation of state of water[14]. This technique differs from ours in that it is based on vibrational temperatures and requires calculation of the mole fraction of non-dissociated wa-

ter molecules. However, their results show similarly improved agreement to experiment for the Hugoniot temperatures.

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